

DEVELOPMENT OF A MINIATURE CRYOGENIC QCM FOR LOW TEMPERATURE CONTAMINATION MEASUREMENT

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INTRODUCTION

A need exists in contamination monitoring for a mass monitor which is small in size, has monolayer coverage detectability, is capable of operation to liquid Helium temperature and dissipates a minimum amount of power. As an example, the testing of cryogenically cooled telescopes for scattering effects produced by condensed contaminant on optical surfaces could use such a QCM in a correlation of contaminant mass to system degradation. Development of a Quartz Crystal Monitor (QCM) for such an application involves consideration of the effect of crystal size and crystal temperature on the all important parameters: crystal mass sensitivity and maximum mass accumulation range. A considerable body of data exists on these parameters at 25°C and to a lesser extent to near liquid Nitrogen temperatures, but very little data is available at liquid Helium temperature. Additionally, low power dissipation electronics must be developed which not only operate at liquid Helium temperature but which also have "start up" capability after an extended cold soak.

This paper describes the development of a miniature QCM shown in Figure 1 that meets the above needs. The mass sensitivity and the mass detectability are considered analytically and the crystal temperature coefficient and the mass range are shown experimentally to be comparable to larger QCM's operated at ambient (25°C) temperature.

SIZE EFFECT ON CRYSTAL PERFORMANCE

Mass Sensitivity

In crystals vibrating in thickness shear mode, changes in frequency are directly related to changes in the plate thickness.

$$\frac{\Delta f}{f} = \frac{\Delta t}{t} \quad \begin{array}{l} f = \text{crystal resonant frequency} \\ t = \text{crystal thickness} \end{array}$$

For a crystal placed in a free molecular flux field, (\dot{m}/A), the change in material thickness on the crystal with time is,

$$\frac{\Delta t}{\Delta \tau} = \frac{\Delta m}{\rho_m A_e \Delta \tau} = \frac{\dot{m}/A}{\rho_m} \quad \begin{array}{l} \rho_m = \text{deposited mass density} \\ A_e = \text{active crystal area or} \\ \text{electrode area} \end{array}$$

Since the thickness change is a function only of the unit mass flux and the mass density, the material thickness increases at the same rate regardless of the crystal size in a given flow field and thus the frequency shift rate is the same. The mass sensitivity relationship for crystals in thickness shear vibration is,

$$\frac{\Delta m}{A} = - \frac{\rho_m \left(\frac{V_{tr}}{2} \right)^2}{f^2} \quad \begin{array}{l} V_{tr} = \text{transverse wave} \\ \text{velocity in plate} \end{array}$$

Therefore for the 10 MHz crystals used in this QCM development, the theoretical sensitivity is,

$$S = 4.43 \times 10^{-9} \frac{\rho_m}{\rho_q} \text{ gm/cm}^2\text{-Hz} \quad \begin{array}{l} \rho_q = \text{quartz density} \\ = 2.65 \text{ gm/cc} \end{array}$$

The criteria used in selecting the crystal frequency was monolayer detectability. If, for instance, nitrogen is the condensing gas of interest, monolayer surface coverage represents 8.1×10^{14} molecules/cm² or 3.77×10^{-8} gm/cm² as calculated by the density method. The density of solid nitrogen condensed from the gaseous state has been shown experimentally (Reference 1) to be 0.9 gm/cc. Therefore 10 MHz crystal sensitivity for solid nitrogen is,

$$S_{N_2} = 1.5 \times 10^{-9} \text{ gm/cm}^2\text{-Hz}$$

The monolayer is 3.75 \AA thick and,

$$\Delta f/\text{monolayer } N_2 = \frac{3.77 \times 10^{-8}}{1.5 \times 10^{-9}} = 25.3 \text{ Hz}$$

Thus partial nitrogen monolayer coverage is easily measurable with 10 MHz crystals.

Mass Detectability

Unlike the condensate thickness relationship, the quantity or mass of condensate collected per unit time varies directly as the electrode area. Thus for the same frequency shift, i. e., for the same condensate thickness increase, a

smaller actual mass of condensate is collected as the crystal electrode decreases in size.

$$\Delta m = \frac{\Delta f t \rho}{f} A_e$$

The minimum mass detectable by a crystal for a given minimum resolvable frequency shift will consequently be quantitatively less for crystals with the smallest electrodes.

In the case of a 1/2" diameter crystal with a 1/4" diameter electrode, the mass required for a one hertz frequency shift is 1.4×10^{-9} grams for mass density 2.65 gm/cc condensate whereas for a 1/4" diameter crystal with 0.14" diameter electrode, the value is 4.4×10^{-10} grams.

Mass Accumulation

Thickness shear mode crystals are usually chosen for QCM work since the elastic damping of the deposited material is minimized in this type of vibration. As deposition increases however, a thickness is reached which does provide losses greater than the circuit driving power and vibration ceases. There are indications that this loss is a direct function of thickness rather than total mass on the crystal in which case the maximum mass accumulation will be independent of the crystal size and depend solely on the Q of the oscillator circuit and the damping properties of the deposited material. Since crystal Q is related to the plate diameter to thickness ratio and thickness is specified for a desired frequency, smaller crystals tend to have lower Q's. Therefore, there may be a tendency to reduced collectible material thickness before oscillation ceases. This important parameter was investigated experimentally and the results discussed in a later section.

LOW TEMPERATURE OPERATION

Determination of mass deposition by observing crystal frequency shifts implies either the elimination or the complete understanding of all other crystal stress producing and thus frequency shift producing parameters. These other parameters include equilibrium temperature coefficient, crystal mechanical mount and incident thermal radiation.

The primary source of frequency change in the crystal other than mass deposition is the change produced by crystal temperature change. The temperature coefficient for various crystallographic cuts has been studied extensively and is generally known for the temperatures of interest (Figure 2). Ideally, crystal cuts are chosen for a desired temperature operating range with zero temperature coefficient. The

cancellation of the temperature effect is greatly improved if two crystals of the same cut are placed in the same temperature environment (one crystal shielded from mass flux) and the beat frequency of the two crystals measured. In this way, despite changes in the temperature coefficient with temperature the beat frequency will be essentially unaffected. In practice, exact cancellation is difficult to achieve over large temperature variations; however, the several decade reduction in temperature induced frequency shifts obtainable with careful crystal selection greatly improves mass measurement.

In this study two temperature ranges were of interest; one at temperatures below 40°K and the other from 100 to 200°K.

The selection of crystals for the very low temperature range, i. e., temperature less than 40°K, was based upon the National Bureau of Standards study of crystals at low temperature (Reference 2). This NBS study used 5 MHz crystals; however, the crystallographic cut should control the temperature coefficient and on the basis of the NBS data a cut of 40°28' was chosen. The temperature coefficient is very nearly constant from LN₂ temperature down to liquid helium temperature as shown in Figure 3. Unfortunately the NBS reference presents data just slightly in excess of LN₂ temperature and in this region most of the crystal cuts shown, including the 40°28' cut, exhibit radical slope changes and reversals in their temperature coefficients.

This is not considered to be a limitation on the usefulness of the crystal since in applications requiring less than 40°K temperature, wide temperature variations are rarely encountered and simply means another crystal cut must be chosen for other applications at higher temperatures.

One common class of earth orbiting satellite experiences temperature excursions in the 100°K to 200°K temperature range. Therefore a crystal cut of 37°03' was chosen for testing since this cut minimizes the overall temperature induced frequency shift in this region as shown in Figure 3.

The crystals used were 1/4" in diameter with 0.14" diameter electrodes. Vacuum deposited aluminum was used as the electrode material for all crystals in order to minimize thermal irradiance induced effects.

In order to avoid mounting stresses caused by differential contraction during temperature changes, the crystals were mounted on three stainless steel springs which also acted as electrical leads.

Crystals at 10 MHz fundamental frequency were used to obtain high sensitivity. Capacitance problems make long leads at this frequency undesirable; therefore, a hybrid chip with sensing crystal oscillator, reference crystal oscillator and a frequency mixer was developed which could be located immediately adjacent to the crystals. In this location,

ever, the hybrid chip must dissipate a minimum amount of power for two reasons: first, the dissipated power may raise the crystal temperature above the condensation temperature of the gas of interest; and secondly, an unacceptably high heat load may be imposed upon the refrigeration system. Low heat dissipation means, however, minimal hybrid chip temperature rise; thus the transistors, etc., must operate at near liquid helium temperature. One compensating factor is the fact that the Q of the crystal increases as the temperature decreases, partially offsetting the drop in output of other components. The hybrid chip developed for this unit dissipates approximately 25 milliwatts with 5 volt input voltage. Its performance over a wide temperature range is reported later.

TEST PROGRAM

The complete QCM was mounted on a copper button at the cryotip of an AIRCO Model LT-3-110 Liquid Transfer Cryo-Tip Refrigerator. The temperature at the base of the QCM as well as the cryotip temperature was sensed by Chromel vs Gold-0.07 at. % iron thermocouples and measured by a HP 419A micro-voltmeter with LN₂ reference junction. The QCM beat frequency output was measured by a HP 5245L frequency counter and recorded on a HP 5050B printer. The beat frequency wave shape was monitored continuously on a Tektronix 453 oscilloscope to observe any erratic behavior.

The initial test was performed on a QCM with 37°03' crystals, intended for the 100°K to 200°K region therefore liquid nitrogen was used as the coolant. Test results are shown in Figure 4, Run 1. The QCM was operated in the cooldown phase at 5 volt input to the oscillators. The observed frequency shift with temperature from 300°K to 80°K of 206 Hz shows an excellent crystal match since a single crystal frequency excursion is 8400Hz in the same temperature range (Figure 3). The effect of input voltage on hybrid chip operation was tested at LN₂ temperature and indicated some frequency dependence on the voltage. The QCM was operated during the warming cycle with 7 volt power until a temperature of 134°K was reached at which time the voltage was dropped to 5 volts.

During the cooling cycle, a very small air leak was permitted to deposit condensibles on the cryotip. These condensibles did not affect QCM performance since the mount shielded the crystals from direct impingement of the air until condensibles could deposit on the colder cryotip. During the warming cycle, however, the cryotip is purposely heated by an integral resistance element resulting in tip temperatures higher than the crystal temperature and the transfer of condensibles from the cryotip to the QCM. As indicated in Figure 4, this process resulted in a frequency change of 190,530 Hz without noticeable beat frequency wave shape distortion. Thus the small crystal is capable of operation with a mass accumulation that results in

a frequency shift of 2% of its fundamental frequency. The first of the mass accumulations shown in the data is probably CO_2 and the second, H_2O based on vapor pressure considerations although gas specie identification measurements were not taken.

The second test of the same QCM was performed with liquid helium cooling. The QCM was operated at 12 volts during cooling and during most of the warming cycle. The test cell was maintained at a high vacuum and no mass accumulation was noted during warmup.

The third test involved the crystals intended for very low temperature operation with a crystal cut of $40^\circ 28'$. The test data is shown in Figure 5. During cooling, 12 volt power was supplied and 5 volts used throughout the warmup. Mass was again allowed to accumulate on the crystal during warmup to illustrate mass loading capability. Some frequency dependence on voltage was shown by the crystals at low temperature as indicated by differences in the 5 volt and 12 volt curves. However, below 20°K where these crystals will find their major usefulness, there is very good agreement. A comparison of the QCM two-crystal beat frequency variation with temperature compared to the NBS single crystal data is shown on Figure 6. The two crystals chosen at random for this experimental set apparently have nearly identical temperature characteristics in the 36°K to 78°K range but exhibit some deviation from 36°K to 5°K . From Figure 6, it is observed that the total temperature induced frequency change from 78°K to 5°K is less than the frequency change represented by a single monolayer of condensed nitrogen. Therefore, this QCM can measure mass changes comparable to partial monolayer coverage with minimal concern for temperature effects particularly if the QCM is held at a fixed temperature, e. g. 10°K .

CONCLUSIONS

Crystal mass sensitivity has been shown to be uninfluenced by crystal size and crystal mass detectability increases with decreasing electrode size. The mass accumulation range on the small crystals used in this program is in excess of 2% of the fundamental frequency which is equivalent to accumulations on crystals with twice the diameter.

The crystal cuts chosen for the two temperature ranges of interest performed as expected with excellent temperature coefficient cancellation down to 5°K .

The miniature cryogenic QCM thus has attributes which should result in partial monolayer measurement at liquid helium temperatures.

ACKNOWLEDGMENTS

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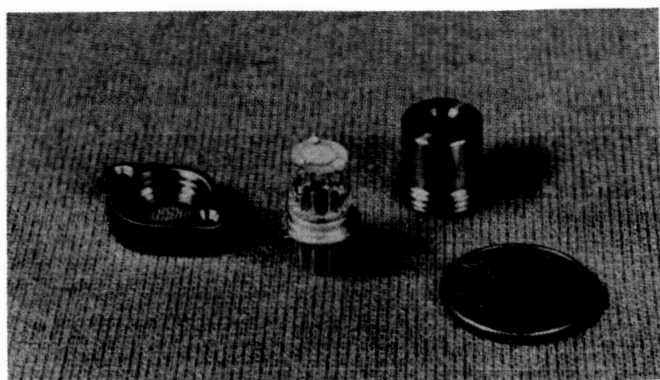


Figure 1—Miniature, Cryogenic QCM

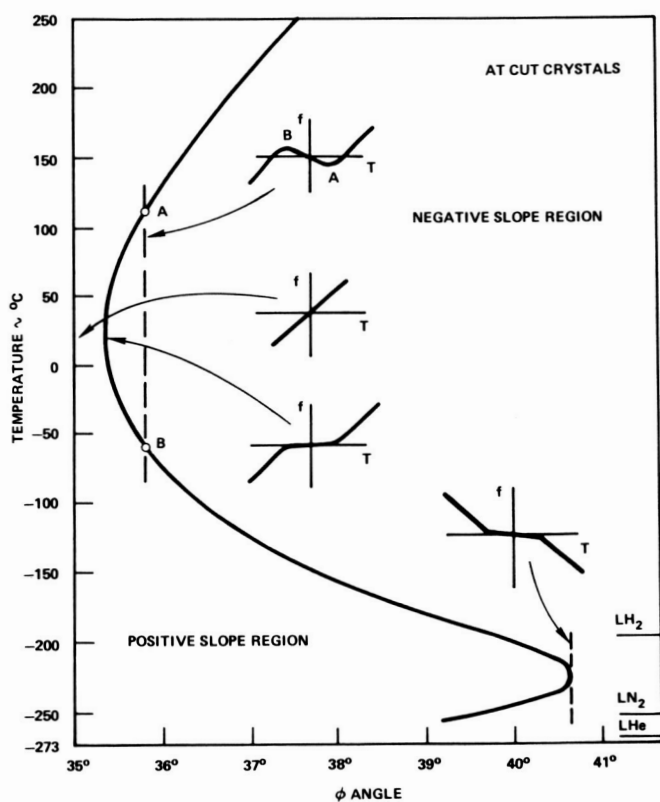


Figure 2—Temperature of Zero Temperature Coefficient of Frequency vs ϕ

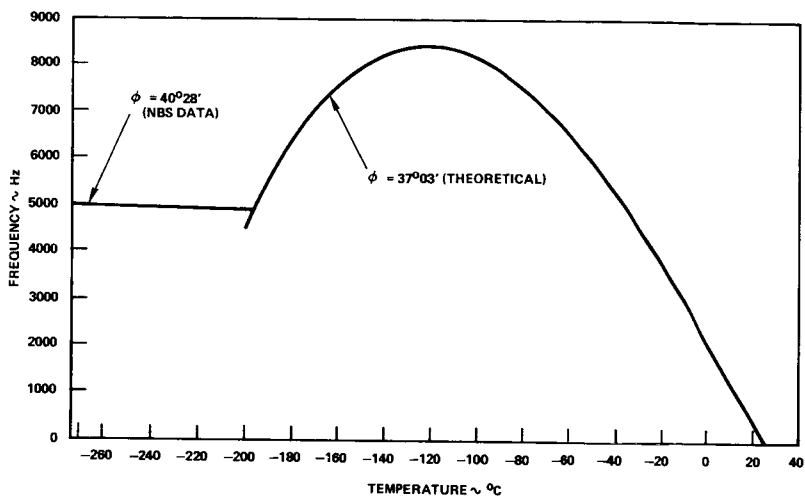


Figure 3—Temperature Coefficients for $\phi = 37^{\circ}03'$ and $\phi = 40^{\circ}28'$ Crystals

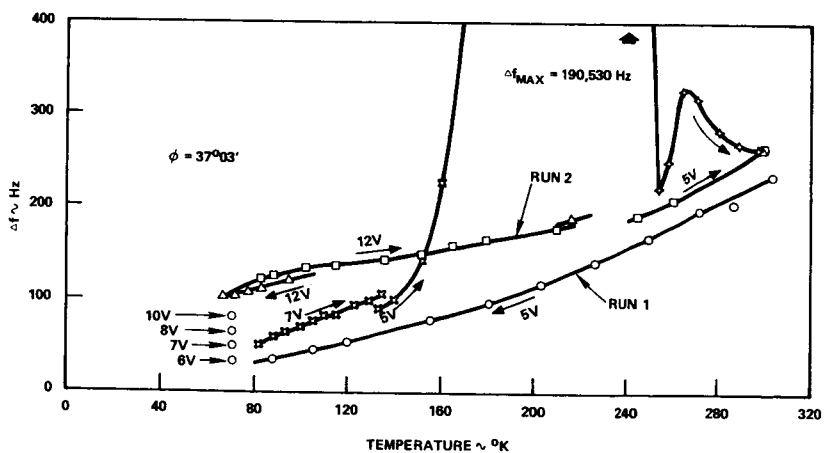


Figure 4—Temperature Coefficient and Mass Accumulation Test of $\phi = 37^{\circ}03'$ Crystal

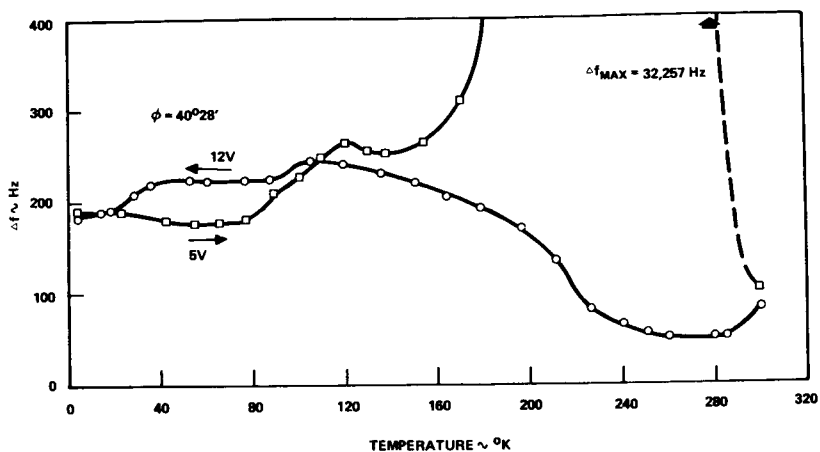


Figure 5—Temperature Coefficient and Mass Accumulation Test of $\phi = 40^{\circ}28'$ Crystal

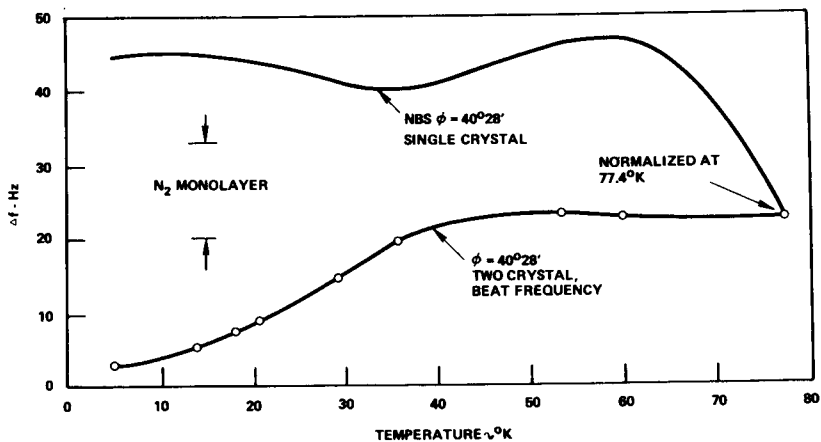


Figure 6—QCM Two Crystal Beat Frequency and NBS Single Crystal Frequency at Low Temperature